

REMOVAL OF ORGANIC SULFUR FROM COAL
BY SUPERCRITICAL EXTRACTION WITH ALCOHOLS

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INTRODUCTION

Growing concern over environmental effects of acid rain has resulted in increased interest in development of pre-combustion removal of sulfur from coal. Physical coal cleaning processes are effective for pyritic sulfur removal but do little to reduce the organic sulfur content of coal. This paper reports the selective removal of organic sulfur from coal, employing ethyl or methyl alcohols as the solvent/reactant. The process is based on the observation that, under supercritical conditions, organic sulfur is selectively removed from the coal matrix. The concentration of sulfur in the resulting solid product is thus reduced, while maintaining over 50% of the concentration of volatile matter compared to that of the parent coal. In addition to the desulfurized solid product, a high BTU gas is produced, and some conversion of coal to liquid products occurs.

LITERATURE REVIEW

Most work on supercritical extraction of coal reported in the literature has as a primary objective the maximum conversion of coal to liquid products. A 1975 article by Whitehead (6) [one of the first references to supercritical coal extraction presented in the literature] presented data on supercritical extraction of coal by coaltar or petroleum naphtha fractions. Tugrul and Olcay (5) reported in 1978 extraction yields and analytical results obtained by supercritical-gas extraction of 250 mesh lignite. They found extraction nearly complete after 30 minutes; extract yields of about 24% were reported. Gas chromatography/mass spectrometry analyses of several extract fractions indicated dozens of paraffins, alkylated hydrocarbons, phenolic and oxygenated compounds; however, no sulfur compounds were reported. A kinetic study of a high-volatile bituminous coal utilizing supercritical toluene was reported by Slomka and Rutkowski (4). A close fit of their experimental data on time dependence of extraction yield was found when a second order equation was used. The use of supercritical toluene extraction of coal in pilot plant studies supported by the British Coal Board was reported by Maddocks (2). The major objective of that study was also maximum conversion of coal to liquid products; reduction of sulfur in the unconverted solid was not reported.

Some work has been reported utilizing alcohols for supercritical extraction of coal. Makabe et al (3) reported extraction of coal with ethanol-sodium hydroxide with the objective of maximizing extraction yield; no sulfur data was reported. Methyl alcohol reaction with a low volatile Bituminous West Virginia coal at higher temperatures (460-600C) was reported by Garner et al (1). Promotion of coal gasification was the objective of that study; sulfur content of the resultant char was not reported.

In contrast to the previous reported work utilizing supercritical solvent extraction of coal, where major objectives have been the conversion of coal to liquid or gaseous products, the major objective of our research effort is to develop a desulfurization process that will result in a solid product suitable for combustion in existing coal fired utility boilers.

EXPERIMENTAL

Batch reactor studies

These experiments utilized a 300cc stirred autoclave reactor; a flow chart of the reactor is given in Figure 1. The coal, previously dried and ground to the desired particle size (generally -40 mesh), is charged to the reactor and alcohol is added. Heating the stirred mixture to above the critical temperature and pressure of the solvent (for ethyl alcohol 243C and 63 atm) results in a sequence of extraction and reaction processes that remove organic sulfur from the coal. After the desired reaction time (generally one hour) the fluid phase is vented from the reactor through a condenser system and liquid and gaseous products are collected. After cooling, the solid product is collected from the reactor.

For some experiments, treatment of the coal with KOH was utilized; two procedures were employed: a) charging the KOH to the reactor (5% of the weight of the coal charged) or b) soaking the coal for ten minutes in a 5% KOH/alcohol solution, followed by alcohol washes to remove essentially all of the potassium from the coal prior to supercritical reaction.

Semi-continuous reactor studies

The flow chart for the semi-continuous Berty gradientless reactor, equipped with a Magnedrive impeller and internal recirculation system, is given in Figure 2. The ground coal is held in a basket within the reactor, while solvent is pumped continuously through the system. After cooling following a run, the solid product is removed from the reactor basket for weighing and analysis. It is possible to maintain a constant pressure in this system, in contrast to the batch system where pressure increases during the course of a run, final pressure being determined by the temperature and charge size to the reactor.

RESULTS AND DISCUSSION

Batch reactor results

For one set of experiments, a comparison of ethyl and methyl alcohols as supercritical extractants was made over a temperature range of 275-450C, utilizing three different coals of varying ratio of organic to pyritic sulfur content. The coals were provided by the State of Illinois Geological Survey, and have been kept under a nitrogen atmosphere since the initial size reduction following mining of the coal. The organic sulfur/pyritic sulfur ratio varied from 0.72 to 2.82 for these coals. For all runs, the reaction time was 1 hr and a solvent/coal ratio of 1/1 was used. The results of these batch runs are summarized in Figure 3, where the sulfur reduction obtained (evaluated on a concentration basis, comparing the total sulfur in the product char to that of the original coal) is shown as a function of the organic sulfur/pyritic sulfur ratio of the original coal, with temperature as a parameter. Ethyl alcohol resulted in greater desulfurization (48%) than methyl alcohol at

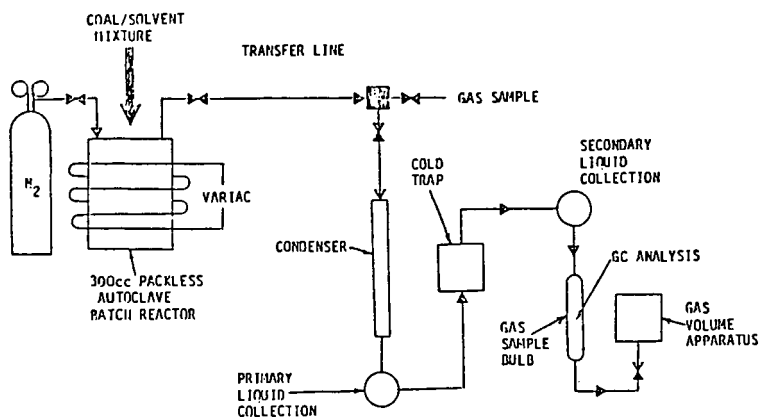


Figure 1. Flow diagram of batch reactor system.

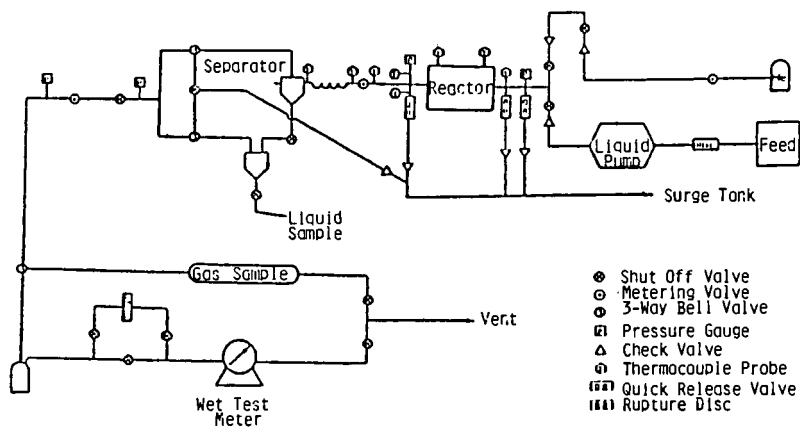


Figure 2. Flow diagram of semi-continuous reactor system.

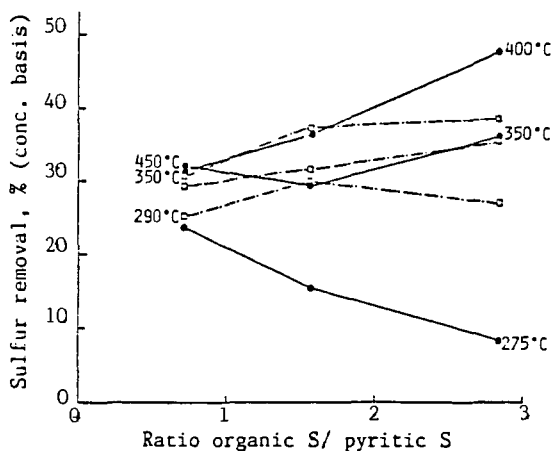


Figure 3. Comparison of ethyl and methyl alcohols as supercritical desulfurization fluids, for coals of varied organic sulfur/ pyritic sulfur ratio. (ethanol —, methanol ----)

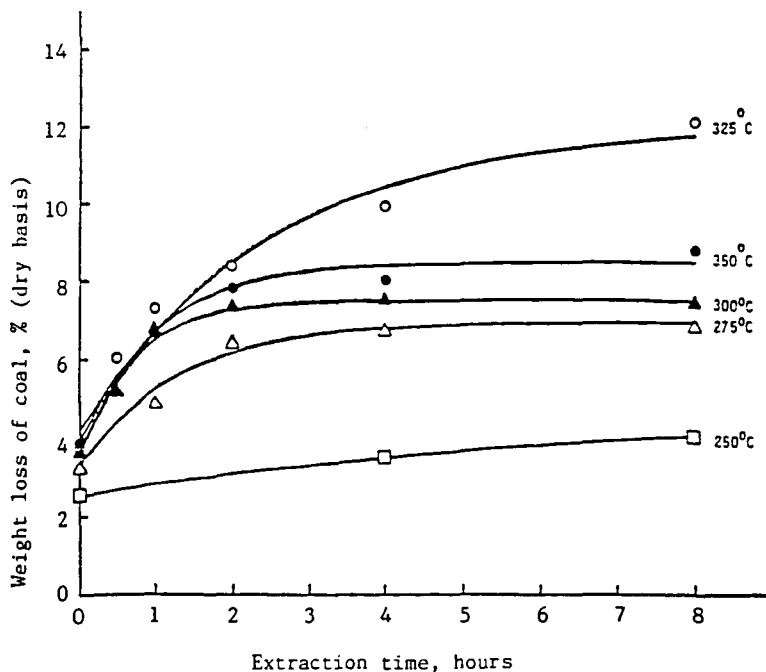


Figure 4. Weight loss of coal as a function of reaction time, semi-continuous reactor.

higher temperatures (400 C) with the higher organic sulfur content coal, and methyl alcohol gave comparable desulfurization to ethyl alcohol at the lower temperature investigated (300 C) with the lower organic sulfur content coal. The results confirm that organic sulfur is being removed by the supercritical extraction/reaction process.

Another series of four runs was performed to compare methyl and ethyl alcohols as supercritical fluid reactants, with and without KOH (5% of the coal charge). Previous studies had indicated enhanced desulfurization by pre-treatment of the coal with a potassium hydroxide-alcohol solution. Reaction time was 2 hours at a reaction temperature of 340C; maximum reaction pressures were 2500 to 4450psig. The high organic sulfur content coal (total sulfur content 4.23%, organic S/pyritic S ratio = 2.82) was used for these runs; results are summarized in Table 1.

Inspection of Table 1 indicates that addition of potassium hydroxide decreased solid product and liquid recoveries, and increased gas production; this was an anticipated result due to the reported influence of caustic on decomposition rates of alcohol at the reaction temperatures utilized. The greatest desulfurization (54.0% reduction in sulfur concentration) resulted in the methanol-KOH system. It is of interest to note that from 56 to 69% of the volatile matter is retained in the solid product compared to that of the original coal. Heating values of the solid products are one to seven per cent greater than the original coal, in spite of a slight increase in ash content. The higher ash resulting from the KOH treatment reflects the greater conversion of coal, as well as the KOH itself. Prior work with both the batch and semi-continuous systems established that comparable desulfurization is attained by both the KOH addition and pre-treatment soaking procedures.

Semi-continuous reactor results

A series of runs were performed using an Illinois No.6 coal having a total sulfur content of 3.0% and an organic S/pyritic S ratio of 2.43. Operating pressure was kept constant at 1750 psig, run temperatures covered the range of 250-350C, and extraction times at run temperature were up to eight hours. The observed weight loss of coal and sulfur removal as a function of extraction time are plotted in Figures 4 and 5, respectively. The conversions indicated at time zero on these plots represent extraction and/or reaction that occurs during the pre-heating time to reaction temperature.

An empirical first order kinetic model was used to fit the experimental data of the percent of coal extracted and the percent of sulfur removed, where concentrations remaining are based on the ultimate extractability at reaction conditions. An Arrhenius plot (Figure 6) reveals that the activation energy for coal extraction was about 30 K cal per mole and for desulfurization was about 17 K cal per mole, which compares favorably with the data in the literature. The selectivity of sulfur removal, as defined by the ratio of sulfur removal to coal extracted, was in the range of 2 to 4.

Gas and liquid product analyses

Analyses of the gas products resulting from the batch experiments reported in Table 1 are given in Table 2. The greater production of hydrogen resulting when KOH was used is evident for both the ethanol and methanol systems. As anticipated, no ethylene and much less ethane resulted from the methanol runs, compared to

TABLE 1

BATCH EXPERIMENTAL DATA

	Standard Coal C-22440	Ethanol, No KOH	Ethanol, 5% KOH	Methanol, No KOH	Methanol, 5% KOH
Maximum Reaction pressure (psig)		2500	3000	2650	4450
Char yield (% of coal charged)		83.0	81.9	89.5	86.8
Liquid yield (% of liquid charge)		83.5	74.8	90.3	59.8
Gas produced, l		10.0	13.0	6.2	26.8
% desulfurization (conc. basis)		36.3	37.6	30.5	54.0
Solid analyses (moisture free)					
% Volatile matter	41.6	23.8	23.2	28.8	25.0
% Ash	10.43	12.18	17.40	11.34	17.89
Btu/lb	12,375	13,263	12,990	12,826	12,501

Reaction Conditions: 60g coal, 60g ethanol, 2 hr. reaction at 340°C.

TABLE 2

GAS ANALYSIS (VOLUME %),
BATCH EXPERIMENTAL DATA

GAS PRODUCTS	ETHANOL		METHANOL	
	NO KOH	5% KOH	NO KOH	5% KOH
H ₂	9	17	4	38
CH ₄	35	23	68	31
C ₂ H ₄	1	1	0	0
C ₂ H ₆	30	27	7	3
CO ₂	20	22	17	25
Other	5	10	4	3

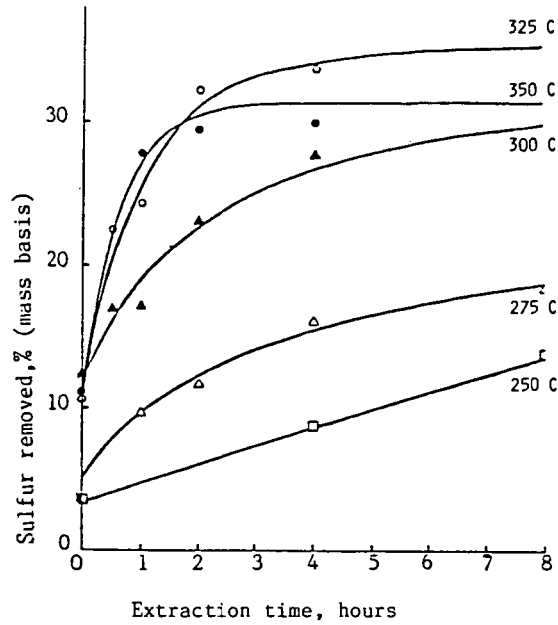


Figure 5. Sulfur removal (mass basis) as a function of reaction time.

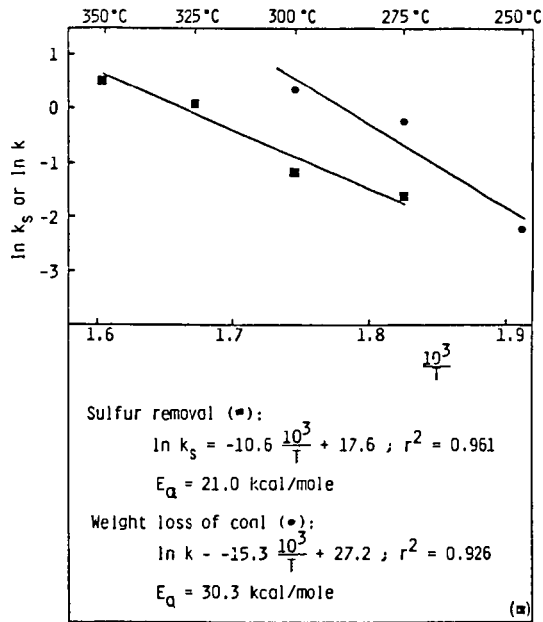


Figure 6. Arrhenius plot of weight loss of coal and sulfur removal data, semi-continuous reactor.

the ethanol runs; methane concentration was higher in the methanol runs.

Gas chromatograms of the liquid products resulting from two of the batch experiments reported in Table 1, where ethyl and methyl alcohols were used without KOH addition, are given in Figures 7 and 8, respectively. A capillary column was used for the analyses, and the sample was split to two different detectors after passing through the column, giving dual traces on each chromatogram. A flame photometric detector (FPD), specific for sulfur containing compounds, and a flame ionization detector (FID), sensitive to essentially all organic compounds, were used. Of the more than half dozen major sulfur containing compounds indicated in Figure 7, several have been identified; ethyl sulfide, ethyl disulfide, thioacetal, and thiophene were indicated by GC/MS analysis. The participation of the ethanol solvent (or a two carbon degradation product) in the desulfurization reactions is suggested by the structure of the sulfur containing products thus far identified. The gas chromatogram of the liquid product from the methanol run indicates only two major sulfur compounds, and lesser amounts of coal derived organic material, compared to the ethanol run.

CONCLUSIONS

It is apparent from the data thus far obtained that both ethyl and methyl alcohols are effective for desulfurization of high organic sulfur content coals when used as extractants/reactants under supercritical conditions. Since it is not known at this time if any significant amount of pyritic sulfur is being removed during the supercritical desulfurization reactions, this possibility must be recognized in any proposed model of the system. Figure 9 presents possible reaction pathways; the extent to which each may be contributing to the overall desulfurization observed under supercritical conditions has yet to be determined.

The potential for processing a typical high sulfur coal to produce a solid product with less than 1% total sulfur by a sequence of physical beneficiation for pyrite reduction, followed by supercritical extraction for removal of organic sulfur, is indicated by example in Figure 10. A 3% total sulfur coal, containing equal amounts of pyritic and organic sulfur, could be processed by existing technologies for removal of pyritic sulfur to give a total sulfur concentration of, say, 1.8%. An additional 50% reduction of the remaining total sulfur would then give a final total sulfur concentration of 0.9%. The initial attempt to attain this goal is also represented in Figure 10, where a coal processed by froth flotation was then subjected to supercritical extraction with the methanol-KOH system at 350C for one hour in the batch reactor. Although the final product total sulfur concentration of 1.37% fell short of the 1% goal, this initial result is encouraging in view of the fact that the froth flotation step has not yet been optimized for the coal used.

ACKNOWLEDGMENTS

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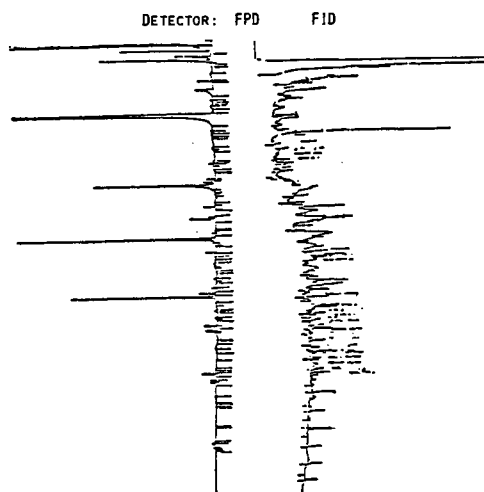


Figure 7. Gas chromatogram of liquid product from supercritical desulfurization of coal with ethanol at 350C. Flame photometric detector (FPD) response is on left; flame ionization detector (FID) response is on right.

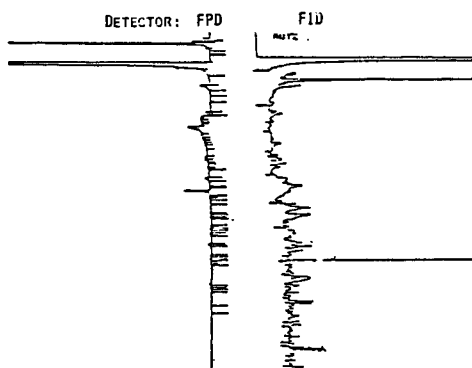


Figure 8. Gas chromatogram of liquid product from supercritical desulfurization of coal with methanol at 350C. Dual detectors as described above.

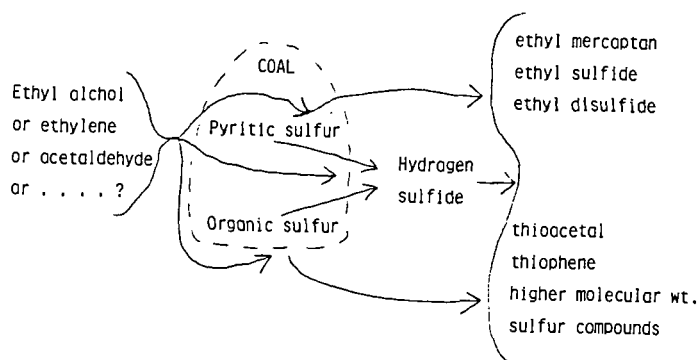


Figure 9. Possible reaction pathways for desulfurization of coal with ethyl alcohol under supercritical conditions.

SEQUENTIAL DESULFURIZATION (EXAMPLE)				
INITIAL EXPERIMENTAL DATA				
	PYRITIC S	ORGANIC S	SULFATE S	TOTAL S
COAL Run of Mine	1.5 %	1.5 %	--	3.0 %
	1.26 %	1.64 %	0.61 %	3.52 %
FROTH FLOTATION	0.3 %	1.5 %	--	1.8 %
	0.95 %	1.47 %	0.34 %	2.76 %
SUPERCritical DESULFURIZATION	0.2 %	0.7 %	--	0.9 %
	0.05 %	0.98 %	0.34 %	1.37 %

Figure 10. Example of sequential processing of coal for removal of pyritic and organic sulfur.

REFERENCES

1. Garner, D.N., W.J. Huffman, and H.W. Parker, Coal Processing Using Methanol as a Reactant. Presented at 79th National Meeting, AIChE, 8th Petrochemical and Refining Exposition, Houston, TX (1975).
2. Maddocks, R.R., J. Gibson and D.F. Williams. Supercritical Extraction of Coal. Chem. Engr. Progress. (June 1979).
3. Makabe, M., Y. Hirano and K. Ouchi. Extraction Increase of Coals Treated with Alcohol-Sodium Hydroxide at Elevated Temperatures. Fuel, vol. 57 (May 1978).
4. Slomka, B. and A. Rutkowski. A Kinetic Study of the Supercritical Toluene Extraction of Coal at 9.8 MPa. Fuel Processing Technology, vol. 5 (1982).
5. Tugrul, T. and A. Olcay. Supercritical-Gas Extraction of Two Lignites. Fuel, vol. 57 (July 1978).
6. Whitehead, J.L. and D.F. Williams. Solvent Extraction of Coal by Supercritical Gases. Journal of the Institute of Fuel, (December 1975).